aqueous ash flows traveling down the bottom slope, such as those described by Fiske (*9*), because the bedded debris at Black Point constitutes the top of the cone. We think that the eruptions here violently blasted vesiculating debris into the water and that the stratification and reverse graded bedding were formed by settling of debris from water over and around the vent. Extreme turbulence of the water and low settling velocities of the vesicular debris could account for the relatively wide lateral dispersal of debris and for the broad flat form of the cone, as compared to subaerial cinder cones.

If explosive submarine pyroclastic eruptions typically build flat-topped cones regardless of depth, then some of the inferences that have been drawn from deep submergence of guyots will have to be reconsidered. Black Point, however, was built within about a hundred meters of the lake surface, and perhaps proximity to the air-water interface was important in determining the form of the cone. We cannot answer this question definitively. However, it would seem, a priori, that if the eruptions broke through to the atmosphere, fragments falling back into the water from the air would exhibit lateral distribution characteristic of products of subaerial eruptions; because this is not the case, a mechanism of sedimentation in turbulent water must still be invoked to account for the observed phenomena. Therefore, it seems probable that the distinctive features of Black Point result from a subaqueous volcano-sedimentary process and that similar volcanic structures might be expected at any depths at which submarine pyroclastic eruptions occur. McBirney (*10*) has introduced thermodynamic arguments to solve the question of possible maximum depths in the oceans of explosive eruptions.

The basaltic cone of Black Point is small compared to guyots, and its exposed parts consist entirely of pyroclastic debris, without any massive flows. The larger submarine volcanoes are undoubtedly more complex both in structure and in form; but where pyroclastic eruptions have played a significant part in their growth, flat-topped structures may be expected, particularly since pyroclastic material is abundant among the volcanic islands of the Pacific and in samples collected from guyots.

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Acid of Krypton and Its Barium Salt

Abstract. *An acid of krypton is formed when krypton tetrafluoride is slowly hydrolyzed by ice at −30° to −60°C. The yield is 2 to 3 percent (mole). A barium salt of this acid, thermally stable at room temperature, is formed by the hydrolysis of krypton tetrafluoride with a 0.35*N *solution of barium hydroxide at 0° to 5°C in a yield of approximately 7 percent by weight.*

The hydrolysis of krypton tetrafluoride, KrF_4, (*1*) like the hydrolysis of xenon tetrafluoride, XeF_4, with water (*2*) leads to its practically quantitative decomposition as follows:

$$KrF_4 + 2H_2O \rightarrow Kr\uparrow + O_2 + 4HF. \quad (1)$$

If the hydrolysis is carried out slowly between −30° and 0°C, the resulting aqueous solution contains a very small amount of an oxidizing species that liberates iodine from acidified iodide solution. The oxidant is not NO_2^- or NO_3^- ion, either of which could form from NO or NO_2 if traces of air leaked into the electrical discharge vessel during the preparation of krypton tetrafluoride (*1*). We now present evidence that this oxidizing substance is an acid of krypton.

In a typical preparation, 100.0 mg (0.63 mmole) of pure krypton tetrafluoride (*3*) were sublimed in a Pyrex glass tube (25 cm long, 1.6 cm inside diameter) and condensed at the bottom of the tube. Water (2.00 g) was distilled into the tube and frozen, in the form of a thin layer, above the krypton tetrafluoride. The tube was kept for 3.0 hours at −30°C, then at −20° to −10°C for 4.0 hours, and finally it was warmed to 0°C. During the first period (−30°C), 0.35 cm^3 (N.T.P.) of gas was evolved; in the next period, during 4.0 hours, 9.40 cm^3 were collected. During the final period, at 0°C, 18.25 cm^3 of gas were obtained; after about 15 minutes, all of the krypton tetrafluoride crystals reacted. The total gas (28.0 cm^3 at N.T.P.) was analyzed (O_2 by Orsat absorption and Kr by heating with Ca and Na to 500°C in a steel tube, and determining the volume and vapor pressure or melting point of the residue) and found to contain 14.2 cm^3 of krypton and 13.8 cm^3 of oxygen. The aqueous solution 2.00 cm^3 contained 47.0 mg HF (determined by titration). These quantitative data substantiate the stoichiometry of Eq. 1.

In addition, the solution contained 0.0183 mmole or 2.9 percent of kryptic acid based on krypton tetrafluoride. The assumption was made that, like xenic acid, kryptic acid oxidizes potassium iodide to iodine according to the equation:

$$KrO_3 \cdot x\,H_2O + 6\,KI + 6\,HCl \rightarrow Kr + 3\,I_2 + 6\,KCl + (3 + x)\,H_2O \quad (2)$$

In a similar experiment, krypton tetrafluoride was hydrolyzed yielding a solution containing 3.90 mmole of hydrogen fluoride and 0.021 mmole of kryptic acid, or a yield of 2.2 percent (mole) based on krypton tetrafluoride; the gas evolved during the hydrolysis contained 51.6 ± 1.5 percent (mole) krypton and 49.6 ± 0.5 percent (mole) of oxygen values, in agreement with Eq. 1.

The questions whether our kryptic acid has the formula $Kr(OH)_6$ comparable to $Xe(OH)_6$ for xenic acid, or H_2KrO_4, in analogy to selenic or some other acid, and whether it contains the krypton in VI-, VIII- or IV-valence state, are as yet undecided; until these are decided, we in our laboratories refer to the acid as "cryptic acid."

Like barium xenate (*4*), a barium salt of a kryptic acid would also be expected to be practically insoluble in water and the yield of the kryptate would be increased in alkaline solutions.

This proved to be the case. In an experiment 76.5 mg of krypton tetrafluoride (0.48 mmole) were hydrolyzed at 0° to 5°C with 50.0 cm^3 of 0.346*N* barium hydroxide solution. The reaction proceeded with the evolution of gas and the formation of a white precipitate of barium fluoride, BaF_2, and barium kryptate. After completion of the reaction, the precipitate was filtered off, washed with small amounts of ice water, and dried (all at 0°C). The weight of the dry precipitate was 181.5 mg. The filtrate was titrated for unreacted barium hydroxide; the difference was equal to 1.10 mmoles of combined barium fluoride and barium kryptate.

The gas evolved during the reaction was 19.0 cm^3 (at N.T.P.) and it contained 49.6 percent krypton and 50.4 percent oxygen corresponding to 0.425 mmole of the original krypton tetrafluoride. The difference from the original amount of krypton tetrafluoride, or approximately 0.05 mmole, apparently reacted with the barium hydroxide, forming *insoluble* barium kryptate.

The dry precipitate of BaF_2 and barium kryptate showed no noticeable thermal decomposition either at 0°C or at room temperature; it started decomposing at approximately 50°C, and the decomposition was complete at 200°C. The total gas collected was 1.9 cm^3 (N.T.P.); if the decomposition is assumed to be as follows:

$$BaKrO_4 \rightarrow BaO + Kr + 1.5\ O_2, \quad (3)$$

this amount of gas is equivalent to 0.034 mmole or 9.7 mg of barium kryptate. The yield of barium kryptate based on the original amount of krypton tetrafluoride is 7.1 percent (mole); this is in reasonable agreement with the value of approximately 0.05 mmole from the krypton recovery. Furthermore, the total barium fluoride formed from the original krypton tetrafluoride should be 0.96 mmole or 168.3 mg and with the weight of barium kryptate (about 9.7 mg) the total weight (178 mg) is in reasonable agreement with the weight of the combined barium fluoride and kryptate actually recovered (181.5 mg), when consideration of the washing is taken into account. Small amounts (about 1 percent or less) of barium carbonate are also present in the precipitate. The amount of barium oxide produced by thermal decomposition was determined by titration and was also in agreement with Eq. 3.

In another experiment, the yield of barium kryptate was determined by reacting it, in hydrochloric acid solution, with potassium iodide solution and back-titrating with standard thiosulfate solution (*4*). If the reaction is

$$BaKrO_4 + 8\ HCl + 6\ KI \rightarrow BaCl_2 + 6\ KCl + 3\ I_2 + Kr + 4\ H_2O \quad (4)$$

the yield equals 9.0 percent (mole) of the original krypton.

Barium kryptate was further identified by isolating the *krypton* formed in the thermal decomposition and identifying it as such by (i) determining the vapor pressure of the pure gas evolved, (20 mm at 90°K and 2 mm at 77°K identical with an authentic sample of krypton, xenon at the same temperatures has a vapor pressure of 0.05 mm and 10^{-3} mm) and (ii) by mass-spectrometer analysis, which showed nearly 100 percent krypton. Thus the presence of barium xenate is excluded.

The alkali salts of kryptic acid can be expected to be even more stable thermally than barium kryptate, in analogy to the corresponding xenates or perxenates (*4, 5*). Thus it may be expected that krypton, like xenon (*4*), may be found in nature not only in the atmosphere but in hydrothermal minerals and in waters of the ocean.

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Pleistocene Chipped Stone Tool on Santa Rosa Island, California

Abstract. *Santa Rosa Island, California, has been the site of numerous discoveries of evidence of Pleistocene Man. The recent finding of a well-made chipped stone tool* in situ *in the mammoth beds adds further evidence.*

Since 1946 (*1*), excavations and studies have been made of the Santa Rosa Island formation which contains the charred bones of dwarf mammoths and birds as well as more than 100 "fire areas" suggesting "barbecue pits."

Human bone, found at a depth of 11 m at Arlington Springs, has been dated by Broecker (*2*) as 10,400 years old. It was analyzed for fluorine by Oakley, who reported the bones as fossil (*3*). In a narrow area of about 1000 m along the sea cliffs, more than 40 radiocarbon dates have been secured from five laboratories. These dates spread through the entire range of radiocarbon.

In September 1963, while searching for radiocarbon material, Gordon Fergusson, Rainer Berger (*4*), and I discovered a well-made chipped stone implement 145 mm by 103 mm, projecting about 45 mm from the compact clays of the Tecolote member of the Santa Rosa Island formation (*5*), and at a depth of approximately 2½ m below the grass roots.

The implement was in a small badland type of gully, and lay stratigraphically between two separate mammoth deposits. The upper one, consisting of a few weathered bones, has been known

Fig. 1. Pleistocene chipped Stone tool found at Santa Rosa Island.